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(21) International Application Number: PCT/JP92/00856 (22) International Filing Date: 6 July 1992 (06.07.92) (30) Priority data: 3/195075 10 July 1991 (10.07.91) JP (71) Applicant (for all designated States except US): THREE BOND CO., LTD. [JP/JP]; 1456, Hazama-cho, Hachioji-shi, Tokyo 193 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only) : USAMI, Ikuzo [JP/JP]; 2915-68, Nekoya, Tsukui-cho, Tsukui-gun, Kanagawa-ken 220-02 (JP). KURIHARA, Makoto [JP/JP]; 229-11, Miyazawa-cho, Akishima-shi, Tokyo 196 (JP). HANADA, Minami [JP/JP]; 4-9, Yurigaoka 3-chome, Asou-ku, Kawasaki-shi, Kanagawa-ken 215 (JP). NAKAJIMA, Kunihiro [JP/JP]; 651-5, Oyamacho, Machida-shi, Tokyo 194-02 (JP).		(74) Agent: TANAKA, Akio; Sushitetu Bldg. 5F., 56-3, Higashi-Ikebukuro 2-chome, Toshima-ku, Tokyo 170 (JP). (81) Designated States: BR, CA, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: ADHESIVE COMPOSITION (57) Abstract An adhesive composition for being applied to at least one of thread contact faces of screw members so as to stick said thread contact faces to each other in engaging the screw members with each other for the purpose of locking and sealing the engaged screw members, in which micro-capsules enclosing at least a reactive monomer of a reactive adhesive composition comprising said monomer, a polymerization initiator of the aforesaid monomer and/or an activator of the aforesaid polymerization initiator is dispersed in a binder comprising a photo-hardening resin composition.		

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DESCRIPTION
ADHESIVE COMPOSITION

[RELEVANT TECHNICAL FIELD]

This invention relates to an adhesive composition for being applied to the thread contact face (screw threads) of a screw member such as a screw, bolt and nut for the purpose of locking and sealing up the screw members engaged with each other.

[BACKGROUND OF THE ART]

There have been conventionally known a variety of adhesive compositions for being applied to the thread contact face of a screw, bolt, nut or the like for the purpose of locking and sealing up such screw members engaged with each other. As to the conventional adhesive compositions, slurry-like liquefied or paste-like adhesive compositions made by dispersing micro-capsules enclosing a reactive adhesive and a resin serving as a binder in an organic solvent or water are disclosed in Japanese Pat. Publication SHO 45-11051(B), Japanese Pat. Publication SHO 54-1737(B), Japanese Pat. Publication SHO 52-46339(B), Japanese Pat. Appln. Public Disclosure SHO 1-27684(A), and Japanese Pat. Appln. Public Disclosure SHO 1-128918(A).

These adhesive compositions are aimed at strengthening the mutual adhesive force of the screw members by destroying the micro-capsules when engaging the screw members to permit the adhesive to flow out of the micro-capsules.

However, these adhesive compositions with which the thread contact faces of the screw members are coated are required to be dried. Thus, if the adhesive composition contains an organic solvent, it entails a sanitary problem of generating the gas of the organic solvent in a drying process.

Furthermore, in the case of using the composition containing water, the drying process which is carried out at an ordinary temperature takes much time, and therefore,

requires heating treatment, thereby leading to a problem of losing the stability in preservation of the reactive adhesive contained in the micro-capsules.

On the other hand, Japanese Patent Publication HEI 5 3-8393 discloses an adhesive composition with the object of carrying out the drying process at room temperature for a short time, which composition is made by adding, to a binder such as a monomer or oligomer of a photo-hardening resin which hardens by the action of radiation of ultra-
10 violet rays or the like, micro-capsules containing an opaque filler, a photo-initiator which starts polymerization of the monomer or oligomer when exposing the monomer or oligomer to the radiation, and the polymer thus obtained or its free-radical polymerization initiator
15 which starts polymerization of the oligomer and/or its activator.

Since this adhesive composition has the opaque filler contained in the binder composed of the photo-hardening resin, the radiation such as ultraviolet rays does not
20 reach deep the inside of the binder, and therefore, only the surface part of the binder which is exposed with the ultraviolet rays is polymerized by the photo-initiator. In this state, only the surface part of the adhesive composition is hardened in the form of a film with the
25 inside part kept in its paste state containing the micro-capsules.

That is to say, the adhesive applied to the thread contact face has its inside part kept in its paste state covered with a film layer. Therefore, the tightening
30 resistance generated when thrusting a screw member into its counterpart at the outset lessens. By further screwing up, the micro-capsules are broken to cause the polymerization initiator or its activator to flow out of the micro-capsules so as to subject the polymer, oligomer,
35 and monomer to polymerization reaction with the polymerization initiator or its activator. Consequently, the effects of sticking and sealing up the screw members are heightened.

However, if the thread contact face of the screw member is left coated with the aforementioned adhesive composition for a long time, a part yet to be hardened of the adhesive composition will be hardened owing to 5 sunlight or heat. This adhesive composition entails a disadvantage such that, even when the polymerization initiator or its activator comes out by tightening up the screw member to break the micro-capsules, no polymerization reaction takes place, and consequently, the effects 10 of sticking and sealing up the screw members cannot be brought about.

In addition, since the aforesaid film contains an inorganic filler, it is disadvantageously fragile, so that a paste-like part yet to be hardened of the adhesive 15 composition may come out when carrying the screw member such as a bolt in the stage of distribution.

[DESCRIPTION OF THE INVENTION]

In the light of the above, this invention provides an 20 adhesive composition for being applied to at least one of thread contact faces of screw members so as to stick said thread contact faces to each other in engaging the screw members with each other, which is characterized in that micro-capsules enclosing at least a reactive monomer of a 25 reactive adhesive composition comprising said reactive monomer, polymerization initiator of said monomer and an activator of the aforementioned polymerization initiator, which is added at need, is dispersed in a binder comprising a photo-hardening resin composition.

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[PREFERRED MODES FOR EXECUTING THE INVENTION]

One embodiment of the adhesive composition according to this invention will be described hereinafter.

The adhesive composition according to this invention 35 includes: (1) an adhesive composition in which micro-capsules separately containing a reactive monomer and a polymerization initiator are dispersed in a binder comprising a photo-hardening resin composition, (2) an

adhesive composition in which micro-capsules containing a reactive monomer and a polymerization initiator and micro-capsules containing an activator are dispersed in a binder comprising a photo-hardening resin composition, (3) an adhesive composition in which micro-capsules containing a reactive monomer and a polymerization initiator and micro-capsules containing a reactive monomer and its activator are dispersed in a binder comprising a photo-hardening resin composition, (4) an adhesive composition in which micro-capsules containing a reactive monomer and a polymerization initiator are dispersed together with an activator in a binder comprising a photo-hardening resin composition, (5) an adhesive composition in which micro-capsules containing a reactive monomer and its activator and micro-capsules containing a polymerization initiator are dispersed in a binder comprising a photo-hardening resin composition, (6) an adhesive composition in which micro-capsules containing a reactive monomer and its activator are dispersed together with a polymerization initiator in a binder comprising a polymerization initiator in a binder comprising a photo-hardening resin composition, and (7) an adhesive composition in which micro-capsules containing a reactive monomer are dispersed together with a polymerization initiator and/or its activator in a binder comprising a photo-hardening resin composition.

Also, in place of the photo-hardening resin composition mixed with the polymerization initiator or its activator as noted above, a photo-hardening resin composition containing a functional group of a polymerization initiator or its activator may be used. For instance, a photo-hardening resin composition containing an amino group can be used.

As the reactive monomer used herein, there can be enumerated a reactive vinyl monomer or its oligomer, preferably an acrylic ester monomer or its oligomer, or a meta-acrylic ester monomer or its oligomer. Also, an epoxy resin can be used.

As the polymerization initiator of the reactive monomer, a radical generator, e.g. peroxide such as benzoyl peroxide can be used in a case that the monomer is an acrylic adhesive agent. As the activator of the polymerization initiator, there are amine serving as a redox catalyst of the peroxide or salicylic acid derivative.

In a case that the monomer is an epoxy adhesive agent, amine and salicylic acid may be enumerated as the polymerization initiator of the monomer.

On the other hand, the photo-hardening resin composition used as a binder is obtained by adding a photo-initiator to the well-known resin which is hardened by ultraviolet rays.

By way of example, there may be enumerated (1) a composition in which a reactive vinyl monomer, preferably an acrylic ester monomer or meta-acrylic ester, contains a photo-polymerization initiator such as benzophenone, and (2) a composition in which an epoxy resin contains a photo-polymerization initiator such as onium salt.

Moreover, various kinds of reactive vinyl monomers, epoxy resins and photo-polymerization initiators have been known, and should not be understood as limitative in this invention.

Also, an adhesive composition capable of reducing the resistance involved in tightening up the engaged screw members can be produced by using a photo-hardening resin serving as a binder, such as flexible or rubber-like elastic material. Instead, if a resin having a high glass transition temperature is used, an adhesive composition having great heat-resistance can be produced.

The ratio of the binder composed of the photo-hardening resin to the micro-capsules in the reactive adhesive according to this invention is 70% or less in the total amount of the adhesive composition of this invention. If it is over 70%, sufficient adhesive power cannot be obtained.

According to this invention, a filler, lubricating

agent, and/or coupling agent can be added to the adhesive composition to provide chemical resistance, high adhesive power, and good lubricating properties.

As is plain from the foregoing, according to this invention, since at least the monomer in the reactive adhesive components is enclosed in the micro-capsules, polymerization reaction is achieved by the action of the polymerization initiator or its activator when the micro-capsules are broken by tightening up the engaged screw members applied with the adhesive composition to cause the monomer to come out of the micro-capsules. Thus, locking and sealing-up of the engaged screw members can be fulfilled reliably.

In addition, since the photo-hardening resin composition is used as a binder, the thread contact faces of the screw members can be coated in a short time with the binder including the micro-capsules and soon hardened by being exposed to radiation such as ultraviolet rays at room temperature without being heated. Thus, the adhesive composition of this invention is advantageous from the standpoint of sanitation because it contains no organic solvent, and it does not damage the preservation and stability of the reactive adhesive agent in the micro-capsules because it is not subjected to heat treatment, thereby to enable the screw members to be stuck to each other at a low cost.

Moreover, since the photo-hardening resin composition serving as a binder is completely hardened to preserve and stabilize the micro-capsules, a paste-like part yet to be hardened of the adhesive composition does not come out of the micro-capsules when carrying the screw member applied with the adhesive composition in the stage of distribution. Besides, the resistance generated in tightening up the engaged screw members can be maintained uniform, the scattering in tightening force of the screw members can be eliminated.

The embodiments of this invention will be described hereinafter.

Embodiments 1 - 3:

A processed bolt was obtained by being applied with an adhesive composition obtained by mixing, at the ratio shown in the following Table 1, and dispersing micro-capsules #1 [capsules enclosing bisphenol A dimethacrylate and a radical generator], micro-capsules #2 [capsules enclosing bisphenol A dimethacrylate and DMPT (N,N-dimethyl-P-toluidine : activator)] in THREE BOND 3057D [UV-hardening acrylic resin containing photo-polymerization initiator made by THREE BOND CO., LTD.], and then, being exposed to UV rays (integral does: 600mJ/cm²).

The bolt thus obtained was provided with two flat washers and tightened up in a nut with 29.4 N.m. Then, the breaking torque was measured after the bolt was held tightened for 24 hours at room temperature.

Comparative Example 1:

The breaking torque of an unprocessed bolt provided with two flat washers and engaged with a nut was measured by tightening up the bolt with 29.4 N.m.

Embodiments 4 - 5:

The breaking torque was measured in the same manner as those in Embodiments 1 - 3 noted above, using an adhesive composition obtained by mixing THREE BOND 3057D with the micro-capsules #1 mentioned above, an activator [salicylic acid derivative and DMPT (N,N-dimethyl-P-toluidine)] at the ratio shown in the following Table 1.

Embodiment 6:

There was used a bolt applied with an adhesive composition obtained by mixing THREE BOND 3057D with the micro-capsules #3 [capsules enclosing bisphenol A epoxy resin], aromatic diamine [polymerization initiator made by NIPPON KAYAKU CO., LTD.] and a salicylic acid derivative (activator) at the ratio shown in the following Table 1. The breaking torque was measured by tightening up the bolt in the same manner as those in Embodiments 1 - 3 except that the bolt was held tightened at room temperature for 72 hours.

Embodiment 7:

The breaking torque was measured in the same manner as those in Embodiments 1 - 3 except that SINX (UV-hardening epoxy resin containing a photo-polymerization initiator 5 made by THREE BOND CO., LTD.) was used as a binder.

Embodiment 8:

The breaking torque was measured in the same manner as that in Embodiment 4 except that SINX was used as a binder.

10 Embodiment 9:

The breaking torque was measured in the same manner as that in Embodiment 6 except that dialkylamino-acrylamide (UV-hardening epoxy polymerization initiator) and DAROCURE 1173 (photo-polymerization initiator made by MERCK JAPAN 15 LTD.) were used as a binder. The measured breaking torque data obtained in the aforementioned Embodiments and Comparative Examples will be shown in Table 1 below. In Table 1, the component A means a component for forming a coating film, and the component B means a component 20 serving as an adhesive agent.

[TABLE 1]

		Embodiment 1	Embodiment 2	Embodiment 3	Comparative Example 1			
Binder	Photo-hardening resins	THREE BOND3057D (UV-hardening acrylic resin made by THREE BOND CO., LTD.)	70	50	30	—		
Capsules enclosing:	Polymerization initiator	Micro-capsules #1 (enclosing Bisphenol A dimethacrylate + Radical generator)	15	25	30	—		
	Activator	Micro-capsules #2 (enclosing Bisphenol A dimethacrylate + DMPT)	15	25	30	—		
		Breaking torque (N·m)	31.1	33.6	35.1	23.5		
		Embodi-ment 4	Embodi-ment 5	Embodi-ment 6	Embodi-ment 7	Embodi-ment 8	Embodi-ment 9	
Binder	Photo-hardening resins	THREE BOND3057D (UV-hardening acrylic resin made by THREE BOND CO., LTD.)	50	50	50	—	—	—
	Photo-hardening resins	SINX (UV-hardening epoxy resin made by THREE BOND CO., LTD.)	—	—	—	50	50	—
	Photo-hardening resins	Dialkylamino-acrylamide (UV-hardening epoxy polymerization initiator)	—	—	—	—	—	50
		DAROCURE1173 (Photo-initiator made by MERCK JAPAN LTD.)	—	—	—	—	—	1
		DMPT (N,N-dimethyl-P-toluidine) (Acrylic polymerization activator)	—	1	—	—	—	—
	Activator	Salicylic acid derivative (acrylic resin+Epoxy polymerization initiator)	2	—	2	—	2	—
		Aromatic diamine (epoxy resin made by Nippon Kayaku CO., LTD.)	—	—	15	—	—	—
		Micro-capsules #1 (enclosing Bisphenol A dimethacrylate + Radical generator)	50	50	—	25	50	—
	Capsules enclosing:	Primary components	Micro-capsules #3 (enclosing Bisphenol A epoxy resin)	—	—	50	—	50
		Activator	Micro-capsules #2 (enclosing Bisphenol A dimethacrylate + DMPT)	—	—	—	25	—
		36.8	35.5	51.0	38.2	41.7	53.7	
		Breaking torque (N·m)						

Test of preservation and stability

After a bolt coated with the adhesive composition used in Embodiment 2 was left outdoors for one month and further left in an atmosphere at 40°C for one month, the bolt was provided with two flat washers and kept tightened with 29.4 N.m for 24 hours. Thereafter, the breaking torque thereof was measured, consequently to obtain a good result as shown in Table 2 below.

[TABLE 2]

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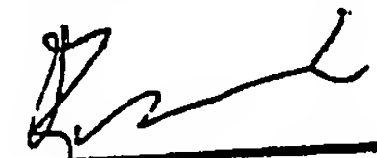
Conditions	Breaking Torque (N.m)
Blank	33.6
Left outdoors for 1 month	33.5
40°C X 1 month	33.6

[INDUSTRIAL APPLICABILITY]

Since at least the reactive monomer in the reactive adhesive components is enclosed in the micro-capsules, polymerization reaction is achieved by the action of the polymerization initiator or its activator when the micro-capsules are broken by tightening up the engaged screw members applied with the adhesive composition to cause the monomer to come out of the micro-capsules. Thus, locking and sealing-up of the engaged screw members can be fulfilled reliably.

[CLAIMS]

1. An adhesive composition for being applied to at least one of thread contact faces of screw members so as to stick said thread contact faces to each other in engaging the screw members with each other, which adhesive composition is characterized in that micro-capsules enclosing at least a reactive monomer of a reactive adhesive composition comprising said reactive monomer, a polymerization initiator of said monomer and an activator of the aforementioned polymerization initiator, which activator is added at need, is dispersed in a binder comprising a photo-hardening resin composition.
2. The adhesive composition according to claim 1, wherein said photo-hardening resin composition has a functional group of said polymerization initiator or its activator.
3. The adhesive composition according to claim 1, wherein said photo-hardening resin composition is composed of a reactive vinyl monomer or an epoxy resin.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 F16B33/06; F16B39/22		
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System Int.Cl. 5 F16B ; C09J		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 077 659 (THOMPSON) 27 April 1983 see claims; examples & JP,A,3 008 393 (THOMPSON) cited in the application ---	1-3
A	GB,A,2 073 610 (THE OAKLAND CORPORATION) 21 October 1981 see claim 1 ---	1-3
A	EP,A,0 409 419 (ACHESON INDUSTRIES, INC.) 23 January 1991 see claims ---	1-3
A	DE,A,2 049 255 (THE NATIONAL CASH REGISTER CO) 22 April 1971 see claims --- -/-	1-3
¹⁰ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
2	Date of the Actual Completion of the International Search 07 OCTOBER 1992	Date of Mailing of this International Search Report 14. 10. 92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer MEULEMANS R.A.M. 

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US, A, 3 746 068 (MINESOTA MINING AND MANUFACTURING) 17 July 1973 see claims -----	1-3

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. JP 9200856
SA 61566**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-0077659	27-04-83	AU-B-	566422	22-10-87
		AU-A-	8929482	21-04-83
		CA-A-	1241144	23-08-88
		JP-B-	3008393	05-02-91
		JP-A-	58125772	26-07-83
		US-A-	4632944	30-12-86

GB-A-2073610	21-10-81	DE-A-	3112631	29-04-82
		US-A-	4325985	20-04-82

EP-A-0409419	23-01-91	CA-A-	2018947	19-01-91
		JP-A-	3089012	15-04-91

DE-A-2049255	22-04-71	BE-A-	684692	30-01-67
		BE-A-	757278	16-03-71
		CH-A-	456254	
		DE-A, B, C	1500856	28-08-69
		FR-A-	2064220	16-07-71
		FR-A-	1503590	
		GB-A-	1096749	
		GB-A-	1253020	10-11-71
		NL-A-	6610873	03-02-67
		US-A-	3485132	23-12-69
		CH-A-	525403	15-07-72
		US-A-	3639137	01-02-72

US-A-3746068	17-07-73	None		
